



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>B05D 1/00, C04B 41/63, C09D 133/00</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 98/52698</b> <b>(43) International Publication Date:</b> 26 November 1998 (26.11.98)
<b>(21) International Application Number:</b> PCT/US98/09707 <b>(22) International Filing Date:</b> 13 May 1998 (13.05.98)  <b>(30) Priority Data:</b> 08/862,274                      23 May 1997 (23.05.97)                      US  <b>(71) Applicant:</b> THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Midland, MI 48674 (US).  <b>(72) Inventors:</b> HARRIS, John, K.; 323 Kent Court, Midland, MI 48642 (US). ROSE, Gene, D.; 216 East Saint Andrews Road, Midland, MI 48642 (US). SCHMIDT, Donald, L.; 2412 Saint Marys, Midland, MI 48640 (US).  <b>(74) Agent:</b> WILLIS, Reid, S.; Patent Dept., P.O. Box 1967, Midland, MI 48641-1967 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> FAST-SETTING LATEX COATINGS AND FORMULATIONS		
<b>(57) Abstract</b>  A fast-setting coating material can be prepared by contacting a stable aqueous dispersion of a polymer that contains strong cationic groups and weak acid groups onto a substrate that is basic or rendered to be basic. Alternatively, the coating material can be prepared by contacting in either order or concurrently, the surface of a substrate with two separate polymers, one of which contains strong cationic groups, and the other of which contains weak acid groups. In this case, the substrate need not be basic for the coating to quickly set.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

## FAST-SETTING LATEX COATINGS AND FORMULATIONS

The present invention relates to a stable aqueous dispersion that forms a water-resistant fast-setting coating when applied to a suitable substrate.

5 Coatings are generally used to provide a protective barrier for applications such as floors, automobiles, exteriors and interiors of houses, as well as painted roads. Protective coatings for floors, for example, have been known since the mid 1950s. Many of the early coating materials were applied using petroleum- or naphthene-based solvents, and as such were undesirable due to the toxicity and flammability of these solvents.

10 Water-based synthetic emulsion compositions such as styrene resin emulsions, styrene-acrylate copolymer resin emulsions, and acrylate emulsions, developed in the early 1960s, gradually replaced organic solvent-based compositions. Although the water-based compositions are preferable to organic solvent-based compositions for safety and environmental reasons, coatings prepared from water-based compositions require long drying times. During drying, the coatings are susceptible to a number of events that may  
15 produce a defective coating, such as drips, sags and runs. Moreover, until the coating is set, it is vulnerable to contamination by dust or water contact, which may also lead to a marred coating. These effects can be minimized by the use of volatile cosolvents which accelerate the drying process, but the cosolvents reintroduce environmental problems that the water-based systems were designed to address.

20 In addition to the environmental concerns, one of the challenges that remains is to develop latexes that coalesce at room temperature, without leaving a tacky surface.

In view of the deficiencies in the art, it would be desirable to provide a coating that rapidly becomes resistant to marring, defects, and contamination during drying, using a stable aqueous dispersion that does not require environmentally unacceptable cosolvents or  
25 crosslinking curatives.

The present invention addresses a need in the art by providing a way to prepare coatings that set quickly upon contact with a substrate. Accordingly, in one aspect, the present invention is a coated material comprising a substrate having a surface and a coating thereupon, wherein the coating is prepared by any of the steps of:

a) contacting the surface of the substrate with a stable aqueous dispersion that contains a polymer having pendant strong cationic groups and pendant weak acid groups; or

b) contacting the surface of the substrate with a stable aqueous dispersion containing a first polymer having pendant strong cationic groups, and a stable aqueous dispersion of a second polymer having pendant weak acid groups, the contact of the polymers with the surface being made in any order or concurrently;

with the proviso that when the coating is prepared by the method of (a), the surface of the substrate is, or is treated to be, sufficiently basic so that the stable aqueous dispersion sets in less time than the time required for a latex that only has pendant strong cation groups or pendant weak acid groups to set.

In a second aspect, the present invention is a method of preparing a fast-setting coating on a substrate having a surface comprising either of the steps of:

a) contacting the surface of a substrate with a stable aqueous dispersion that contains a polymer having pendant strong cationic groups, and pendant weak acid groups; or

b) contacting the surface of the substrate with a stable aqueous dispersion that contains a first polymer having strong cationic groups, and a stable aqueous dispersion that contains a second polymer having weak acid groups, the contact of the polymers with the surface being made in any order or concurrently;

with the proviso that when the fast-setting coating is prepared by the method of (a), the surface of the substrate is, or is treated to be, sufficiently basic so that the stable aqueous dispersion sets in less time than the time required for a latex that only contains pendant strong cation groups or pendant weak acid groups to set.

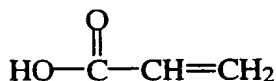
In a third aspect, the present invention is a stable aqueous dispersion comprising a polymer having strong cationic groups, weak acid groups, and structural units formed from the polymerization of a non-interfering monomer, wherein the ratio of structural units formed from the polymerization of the non-interfering polymerizable monomer to strong cationic

groups and the weak acid groups is from 70:30 to 99:1, with the proviso that the strong cationic groups are associated with non-alkaline counterions.

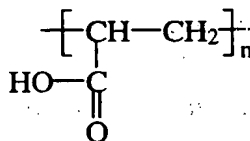
The fast-setting coated material of the present invention can be prepared by contacting a substrate with a stable aqueous dispersion that contains a polymer having structural units formed from the polymerization of: a) a polymerizable strong cationic monomer, and b) a polymerizable weak acid monomer. In this aspect of the present invention, the substrate is, or is treated to be, sufficiently basic that the stable aqueous dispersion sets in a time that is less than the time required for a latex that only contains pendant strong cation groups or pendant weak acid groups to set.

The term "sufficiently basic" refers to sufficiency of amount of base as well as base strength. A coating "sets" or is "dry-to-the-touch" when it has formed a skin with sufficient mechanical integrity such that no portion of the skin is removed when it is touched lightly with a finger, and no portion is washed off the substrate when rinsed under a light stream of water.

As used herein, the term "polymerizable strong cationic monomer" refers to a monomer that contains ethylenic unsaturation and a cationic group having a charge that is independent of pH. Similarly, the term "polymerizable weak acid monomer" refers to a monomer that contains ethylenic unsaturation and an acid group having a  $pK_a$  in the range of 2 to 10. The term "structural units formed from the polymerization of ..." is illustrated by the following example:



Acrylic Acid



Units formed from the polymerization of Acrylic Acid

In addition to structural units formed from the polymerization of a polymerizable strong cationic monomer and a polymerizable weak acid monomer, the polymer also preferably includes structural units formed from the polymerization of a polymerizable non-interfering monomer. The term "polymerizable non-interfering monomer" is used herein to refer to a monomer that does not adversely affect the fast-setting nature of a coating prepared from the stable aqueous dispersion of the polymer.

Polymerizable weak acid monomers that are suitable for the preparation of stable aqueous dispersion used to prepare the water-resistant fast-setting coating include ethylenically unsaturated compounds having carboxylic acid, phenolic, thiophenolic, or phosphinyl functionality. Preferred polymerizable weak acid monomers include acrylic acid, methacrylic acid, itaconic acid,  $\beta$ -carboxyethyl acrylate (usually as a mixture of acrylic acid oligomers), vinylbenzoic acid, and 2-propenoic acid: 2-methyl-, (hydroxyphosphinyl) methyl ester. Acrylic acid and methacrylic acid are more preferred weak acid monomers.

The polymerizable strong cationic monomer is associated with a non-alkaline counterion, which may be, for example, halide such as chloride, bromide, or iodide, as well as nitrate or sulfate. As used herein, the term "non-alkaline counterion" refers to a counterion that does not cause sufficient ionization of the weak acid to render the stable aqueous dispersion unstable. Thus, a bicarbonate counterion would not be appropriate if a carboxylic acid were the weak acid, since this counterion would, in sufficient quantity, raise the pH of the stable aqueous dispersion to an unstable level. For example, for a stable aqueous dispersion containing 2.3 mole percent each of a quaternary ammonium salt and a carboxylic acid, the presence of a sufficient amount of a bicarbonate counterion to raise the pH of the latex to above 5.5 would cause the dispersion to become unstable.

Suitable polymerizable strong cationic monomers include salts of ethylenically unsaturated compounds having quaternary ammonium, sulfonium, cyclic sulfonium, and phosphonium functionality. Examples of suitable monomers having quaternary ammonium functionality include ethylenically unsaturated trialkylammonium salts such as vinylbenzyl tri- $C_1$ - $C_4$ -alkylammonium chloride or bromide; trialkylammoniumalkyl acrylates or methacrylates such as 2-[(methacryloyloxy)ethyl]-trimethylammonium chloride and N,N-diethyl-N-methyl-2-[(1-oxo-2-propenyl)oxy] ethanaminium methyl sulfate (Chem. Abstracts Reg. No. 45076-54-8); and trialkylammoniumalkyl acrylamides such as N,N,N-trimethyl-3-[(2-methyl-1-oxo-2-propenyl)amino]-1-propanaminium chloride (Chem. Abstracts Reg. No. 51441-64-6) and N,N-dimethyl-N-[3-[(2-methyl-1-oxo-2-propenyl)amino]propyl]-benzenemethaminium chloride (Chem. Abstracts Reg. No. 122988-32-3). A preferred polymerizable quaternary ammonium salt is 2-[(methacryloyloxy)ethyl]trimethylammonium chloride.

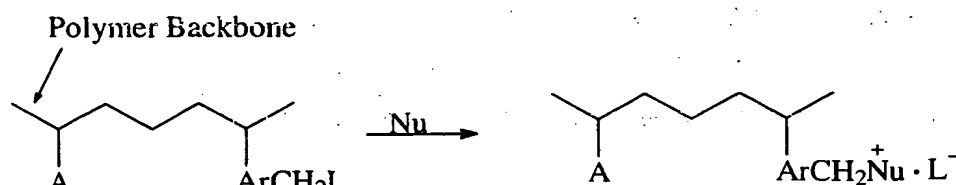
Examples of polymerizable unsaturated sulfonium salts include dialkylsulfonium salts such as [4-ethoxy-3-(ethoxycarbonyl)-2-methylene-4-oxobutyl]dimethylsulfonium bromide (Chem. Abstracts Reg. No. 63810-34-4); and vinylbenzyl dialkylsulfonium salts such as

vinylbenzyl dimethylsulfonium chloride. Examples of polymerizable cyclic sulfonium salts include 1-[4-[(ethenylphenyl)methoxy]phenyl]tetrahydro-2H-thiopyranium chloride (Chem. Abstracts Reg. No. 93926-67-1), and vinylbenzyl tetrahydrothio-phenonium chloride, which can be prepared by the reaction of vinylbenzyl chloride with tetrahydrothiophene.

- 5            Examples of polymerizable phosphonium salts include 2-methacryloxyethyltri- $C_1$ - $C_{20}$ -alkyl-, aralkyl-, or aryl-phosphonium salts such as 2-methacryloxyethyltri-n-octadecylphosphonium halide (Chem. Abstracts Reg. No. 166740-88-1); tri- $C_1$ - $C_{18}$ -alkyl-, aralkyl-, or aryl-vinylbenzylphosphonium salts such as trioctyl-3-vinylbenzylphosphonium chloride, trioctyl-4-vinylbenzylphosphonium chloride (Chem. Abstracts Reg. No. 15138-12-4),  
 10        tributyl-3-vinylbenzylphosphonium chloride, tributyl-4-vinylbenzylphosphonium chloride (Chem. Abstracts Reg. No. 149186-03-8), triphenyl-3-vinylbenzylphosphonium chloride, and triphenyl-4-vinylbenzylphosphonium chloride (Chem. Abstracts Reg. No. 145425-78-1);  $C_3$ - $C_{18}$ -alkenyltrialkyl-, aralkyl-, or aryl-phosphonium salts such as 7-octenyltriphenyl-phosphonium bromide (Chem. Abstracts Reg. No. 82667-45-6); and tris(hydroxymethyl)(1-  
 15        hydroxy-2-propenyl)phosphonium salts (Chem. Abstracts Reg. No. 73082-48-1).

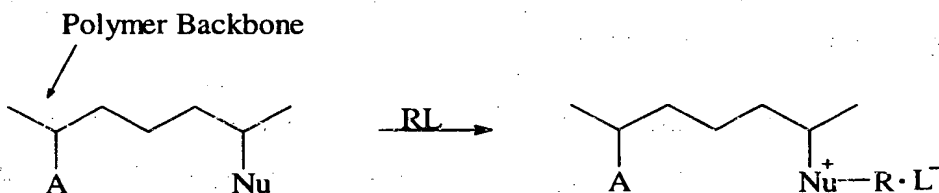
An example of a polymerizable monomer that contains both a weak acid group and a strong cationic group is N-(4-carboxy)benzyl-N,N-dimethyl-2-[(2-methyl-1-oxo-2-propenyl)-oxy] ethanaminium chloride.

- It is possible to add strong cationic functionality to an already prepared polymer. For  
 20        example, a polymerizable monomer having a weak acid group can be copolymerized with a polymerizable non-interfering monomer containing an electrophilic group, such as a vinylbenzyl halide or a glycidyl methacrylate, to form a polymer having a weak acid group and an electrophilic group. This polymer can then be post-reacted with a nucleophile such  
 25        as a tertiary amine or a dialkyl sulfide, which can displace the halide group or oxirane groups and form a benzyonium salt as illustrated:



where A is a pendant weak acid group; Ar is an aromatic group, preferably a phenyl group; L is a leaving group, preferably a halide group, more preferably a chloride group; and Nu is preferably a dialkyl sulfide such as dimethyl sulfide and diethyl sulfide; a cyclic sulfide such as tetrahydrothiophene; or a tertiary amine such as trimethyl amine, triethyl amine, tripropyl amine, tributyl amine, and triethanol amine.

In another example of adding strong cationic functionality to an already prepared polymer, a polymer backbone that contains pendant acid groups and a tertiary amine or a sulfide can be post-reacted with a suitable alkylating reagent such as an alkyl halide to form a polymer that contains acid groups and strong cationic groups:



where RL is an alkylating reagent.

Examples of non-interfering polymerizable monomers include acrylates such as methyl acrylate, ethyl acrylate, butyl acrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, glycidyl acrylate, and allyl acrylate; methacrylates such as methyl methacrylate, ethyl methacrylate, butyl methacrylate, allyl methacrylate, glycidyl methacrylate, 2-hydroxyethyl methacrylate, and 2-hydroxypropyl methacrylate; alkanyl aromatic hydrocarbons such as 4-methacryloxy-2-hydroxy-benzophenone and 2-(2'-hydroxy-5-methacryloxyethylphenyl)-2H-benzotriazole; and C<sub>1</sub>-C<sub>4</sub>-alkyl- or alkenyl-substituted styrenes, preferably styrene,  $\alpha$ -methylstyrene, vinyltoluene, and vinylbenzyl chloride. Other examples of non-interfering species include C<sub>3</sub>-C<sub>18</sub>-perfluoroalkyl methacrylates such as 2-(perfluorooctyl)ethyl methacrylate; C<sub>3</sub>-C<sub>18</sub>-perfluoroalkyl acrylates such as 2-[ethyl[(heptadecafluorooctyl)-sulfonyl]amino]ethyl 2-propenoate; and C<sub>3</sub>-C<sub>18</sub>-perfluoro-alkyl vinylbenzenes. (See U.S. Patent 4,929,666, column 4, lines 54 to 68, and column 5, lines 1 to 30.)

The ratio of the pendant weak acid groups to the pendant strong cationic groups is application dependent, but is generally in the range of 4:1 to 1:4. The ratio of the structural units formed from the polymerization of the polymerizable non-interfering monomer to the

weak acid groups and the strong cationic groups varies depending on the percent solids of the stable aqueous dispersion, but is preferably not less than 70:30, more preferably not less than 80:20, more preferably not less than 90:10, and most preferably not less than 94:6; and preferably not greater than 99.5:0.5, more preferably not greater than 99:1, and most  
5 preferably not greater than 98:2.

In general, the higher the solids content, the lower the concentration of the total ionic species that is required to form the quick-set coatings. The solids content of the stable aqueous dispersion is application dependent, but preferably not less than 10, more preferably not less than 20, and most preferably not less than 30 weight percent, and  
10 preferably not more than 60, more preferably not more than 55, and most preferably not more than 50 weight percent.

The stable aqueous dispersion can be prepared by any suitable means, and is advantageously prepared by the steps of: 1) preparing a seed latex; 2) diluting the seed latex with water; 3) contacting the diluted solution with a radical initiator, a polymerizable  
15 non-interfering monomer, a polymerizable weak acid monomer, and a strong cationic monomer; and 4) polymerizing the solution from step 3 under such conditions to form a stable aqueous dispersion having non-interfering groups, pendant strong cationic groups, and pendant weak acid groups.

The seed latex is preferably prepared by emulsion polymerization in a batch process using a cationic surfactant. The seed latex acts as a locus of polymerization for subsequent  
20 monomer addition; so that the formation of new particles is minimized and greater uniformity in the distribution of particle size in the final product is achieved. Thus, the monomer or monomers used to prepare the seed latex are chosen to form particles that have an affinity for the monomers subsequently added, so that polymerization occurs preferentially in or on  
25 the seed latex particles. The extent to which the seed latex is diluted in step 2 is a function of the desired particle size and the percent solids in the final latex, and can be readily determined by one of ordinary skill in the art.

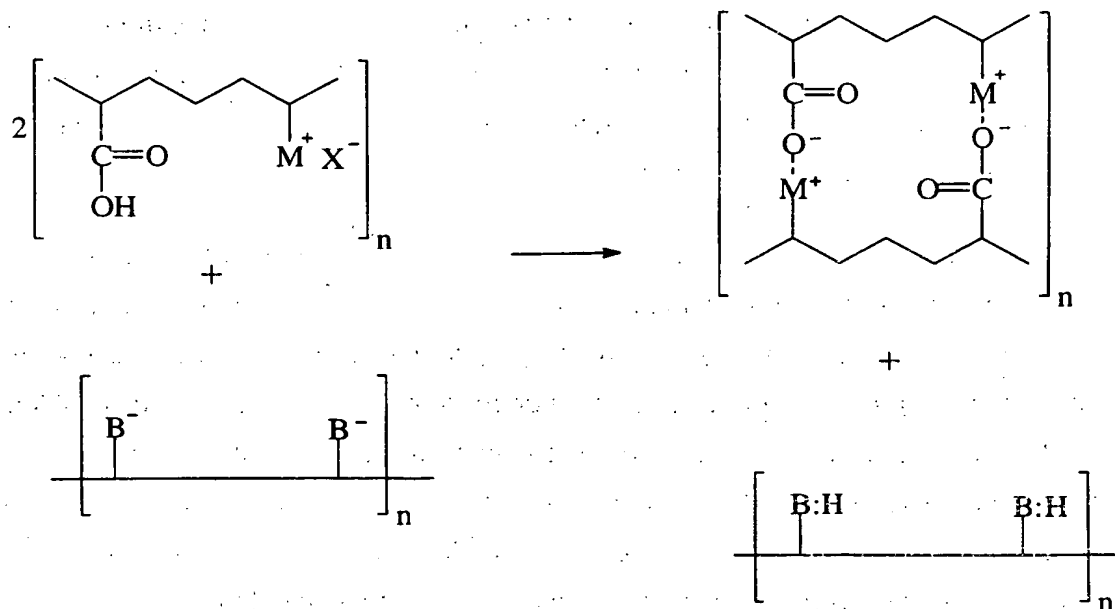
It is also possible to prepare a stable aqueous dispersion from a preformed polymer. The preformed polymer can be dissolved in a suitable solvent, then dispersed in water by  
30 any suitable method. The solvent can then be removed and the solids content adjusted to form a so-called artificial latex.

The stable aqueous dispersion may optionally contain fillers, pigments, dyes, fungicides, bactericides, thickeners, coalescing aids, and defoamers, that do not cause premature coagulation of the dispersion. Fillers may include clays, silica, ceramics, and other stable aqueous dispersions.

- 5           A fast-setting coated material can be prepared when the stable aqueous dispersion that contains the polymer having the strong cationic groups, the weak acid groups, and optionally, structural units formed from the polymerization of the polymerizable non-interfering monomer, is contacted with a substrate having a contact surface which is, or is treated to be, sufficiently basic so that the stable aqueous dispersion sets in less than the
- 10   time required for a latex that only contains pendant strong cation groups or pendant weak acid groups (but not both) to set, preferably within 5 minutes, and more preferably within 3 minutes, and most preferably within 1 minute. The basicity of the substrate required to cause the dispersion to set rapidly depends on the  $pK_a$  of the weak acid groups on the polymer. The lower the  $pK_a$  of the weak acid, the weaker the base required to cause rapid
- 15   setting. The stronger the base and the higher the concentration of the base, the faster the setting.

Though not bound by theory, it is believed that the rapid dry-to-the-touch coating is formed by a coacervation process. In this process, the basic substrate acts as a proton sink by extracting protons from the weak acid groups to form the conjugate base, which can then

20   bind irreversibly and rapidly with the strong cationic group to form an irreversible crosslinking network. This crosslinked network is believed to represent the coating after it has set.



In the above illustration, B<sup>-</sup> is a basic moiety that is associated with the substrate. BH, the conjugate acid of B<sup>-</sup>, preferably has a higher pK<sub>a</sub> than the weak acid (which is a carboxylic acid group in the illustration). However, this need not be the case. For example, if there is a sufficient amount of B<sup>-</sup> present on the substrate, the conjugate acid BH may actually have a pK<sub>a</sub> that is the same as, or lower than, the pK<sub>a</sub> of the weak acid, presumably because once the proton is abstracted by B<sup>-</sup>, the process is irreversible.

An indication of the surface basicity may be provided, for example, by contacting the surface of the substrate with water-wetted pH paper. The pH necessary to induce coacervation will depend on the pK<sub>a</sub> of the weak acid; for a polymer containing pendant carboxylic acid units, for example, the pH of the water in contact with the substrate is not less than 6, more preferably not less than 8, and most preferably not less than 10.

The substrate may be inherently basic. Such substrates include cementitious materials such as Portland cement, aluminous cement, inorganic mortar, or cementitious fiber board. The substrate, if not inherently basic, may be treated to be sufficiently basic to cause the coated material to quickly set. For example, the surface of the substrate may be treated with an aqueous solution having a pH that is greater than the pK<sub>a</sub> of the weak acid, prior to, or concurrent with, the application of the stable aqueous dispersion of the polymer to the surface of the substrate. Such basic aqueous solutions include, but are not restricted to, alkali metal and alkaline earth metal phosphates, carbonates, bicarbonates, and hydroxides.

Preferred substrates that can be treated with base include metal, glass, paper, plastic, cloth, wood, and leather. The substrate may also take a specific shape such as the shape of a hand, for the purposes of forming a latex glove.

5 The substrate may also include a filler material that renders the surface of the substrate sufficiently basic to cause the stable aqueous dispersion of the polymer to form a fast-setting coating. Lime and calcium carbonate are examples of such filler materials.

10 In another embodiment of the present invention, fast-setting coatings can be prepared by contacting a substrate with a first stable aqueous dispersion that contains a polymer having structural units formed from the polymerization of a polymerizable strong cationic monomer; and a second stable aqueous dispersion that contains a polymer having structural units formed from the polymerization of a weak acid monomer. The stable aqueous dispersions may be contacted with the substrate in any order or substantially concurrently, preferably substantially concurrently, and surprisingly, the substrate need not be basic or rendered basic. The second stable aqueous dispersion is preferably stabilized in 15 the presence of an anionic surfactant such as a sulfate, including sodium lauryl sulfate, or DOWFAX EB™ surfactant (from The Dow Chemical Company). The sulfate may also be present as end-groups on the polymer chains resulting from the use of persulfate initiator during the polymerization of the anionic latex. The first and second stable aqueous dispersions are preferably applied to the substrate using a plural component sprayer.

20 Both the first and the second stable aqueous dispersions preferably have structural units formed from the polymerization of the polymerizable non-interfering monomer. The mole percent of structural units formed from the polymerization of the strong cationic monomer in the first stable aqueous dispersion of the polymer is preferably not less than 0.5, more preferably not less than 1, and most preferably not less than 2 mole percent, and 25 preferably not greater than 20, more preferably not greater than 10, and most preferably not greater than 5 mole percent, based on the total mole percent of strong cationic monomer and non-interfering monomer. The mole percent of structural units formed from the polymerization of the weak acid monomer in the second stable aqueous dispersion of the polymer is also preferably not less than 0.5, more preferably not less than 1, and most 30 preferably not less than 2 mole percent, and preferably not greater than 20, more preferably not greater than 10, and most preferably not greater than 5 mole percent, based on the total mole percent of strong cationic monomer and non-interfering monomer.

The coated materials of the present invention have wide applicability, including painted concrete roads, where a fast-setting coating can be prepared in the absence of solvents or crosslinking curatives, by merely applying the stable aqueous dispersion of the polymer (or polymers) to the surface of the road. Other uses include primers for stucco houses or cementitious fiber boards. The aqueous dispersions can also be used to coat cured or uncured cement to reduce water evaporation, thereby improving the physical properties of the final concrete. The dispersions can also be used to prepare latex gloves or condoms by dipping a basic form or mold into the stable aqueous dispersion to cause rapid setting of the dispersion on the form.

10 In the most preferred formulations, the stable aqueous dispersions used to prepared the coated materials have a shelf-stability of at least 6 months, preferably at least one year. The formulations may also contain additives such as pigments, dyes, fungicides, and bactericides.

15 The following examples are for illustrative purposes only and are not intended to limit the scope of this invention.

#### Example 1 - Preparation of a Fast-Setting Clear Coating

The stable aqueous dispersion was prepared in a two-step process. First, a cationic surfactant stabilized polystyrene seed latex was prepared using a batch process. Next, a portion of the seed latex was used in a continuous addition process to prepare a second, film-forming latex containing a carboxylic acid and a quaternary ammonium functional monomer.

The cationic latex seed was prepared in the following manner. To a 1-liter, 3-neck, glass reaction flask equipped with a nitrogen inlet, a reflux condenser with a nitrogen outlet, and a mechanical stirrer, was added styrene (100 g), ARQUAD™ 18-50 octadecyltrimethylammonium chloride surfactant (a trademark of AkzoNobel, 20 g active), hydrogen peroxide (3.3 g, 1.0 g active), water (200 g), and iron sulfate solution (0.25 g in 100 g water). The flask was heated to 70°C over 2 hours with stirring under nitrogen, after which the stirring was stopped and the heating source removed. The latex seed was allowed to sit overnight in the flask. The result was an opaque, high viscosity dispersion with 35.8 percent solids. The particle size was 407 Å (mean value) and 393 Å (median value).

The film-forming latex was prepared from the cationic seed latex using a continuous addition polymerization method. Syringe pumps were used as the continuous addition control means. To a 2-liter, 3-neck, glass reaction flask equipped with a nitrogen inlet, a reflux condenser with a nitrogen outlet, and a mechanical stirrer, was added water (452.3 g) and the cationic seed latex (8.8 g). The flask was heated to 60°C and stirred. Table I shows the solutions that were prepared for continuous addition.

Table I

Stream	Component	Amount
1	Butyl Acrylate	176 g
	Methyl Methacrylate	124 g
	Methacrylic Acid	5.3 g
2	M-Quat <sup>a</sup>	17.3 g (12.8 g active)
3	t-Butylhydroperoxide	1.8 g (1.3 g active)
4	Sodium Formaldehyde Sulfoxylate	0.96 g in 10 mL water

<sup>a</sup> 2-[(methacryloyloxy)ethyl] trimethylammonium chloride obtained as a 74 percent aqueous solution from Bimax Inc., 717 Chesapeake Ave., Baltimore, MD 21225

The components from the four streams were added over the first 4 hours of polymerization. After completion of addition, polymerization was continued at 60°C for 0.5 hour. The resulting latex was filtered and found to have a solids content of 37.0 percent. Table II shows the composition of the latex.

Table II

Monomer	Weight percent	Mole percent	Molecular weight g/mol
Butyl Acrylate	55.3	50.2	128.1
Methyl Methacrylate	39.0	45.3	100.1
Methacrylic Acid	1.7	2.3	86.1
M-Quat	4.0	2.3	207.7

The particle size was 1550 Å (mean) and 1450 Å (median).

A clear, fast-setting coating was prepared by applying a coat of the latex to a cementitious fiber board using a paint brush. The sample was observed at 22.4°C and 65 percent relative humidity. Thirty seconds after application of the latex, the coated, cementitious fiber board was placed under running water. The coating showed no signs of bleeding, running or any detrimental effects. Within 20 minutes of application the latex dried to a clear film.

#### Example 2 - Preparation of a Fast-Setting Pigmented Coating

A titanium dioxide pigment slurry was used to prepare a pigmented latex coating to demonstrate that a fast-setting coating could be obtained on an alkaline surface using pigmented coating formulations. The composition of the titanium dioxide pigment slurry is given in Table III.

Table III

Component	Amount (weight percent) <sup>a</sup>
Water	31.0
Ti-Pure™ R-900 Titanium Dioxide <sup>a</sup>	66.5
RHODAQUAT™ M242C/26 Cationic Surfactant <sup>b</sup>	2.20
FOAMASTER™ V Nonionic Surfactant <sup>c</sup>	0.30

<sup>a</sup> (a trademark of E. I. du Pont de Nemours and Company)

<sup>b</sup> (a trademark of Rhône-Poulenc)

<sup>c</sup> (a trademark of Henkel)

The titanium dioxide pigment slurry was prepared by mixing the titanium dioxide into the water containing the surfactants under high speed shearing to form a smooth, viscous dispersion. To a glass jar was added 29.4 g of this slurry, then 5.5 g of deionized water. The diluted slurry was mixed to form a uniform suspension. The latex having the composition shown in Table II and a total solids content of 37.4 weight percent was then mixed with the slurry at about 350 rpm for 3 minutes. The resulting dispersion had the consistency and color of whole milk. A coating of this dispersion was applied with a paint brush onto a cementitious fiber board. After 1 minute the coating on the board was placed under a stream of running water. There was no indication of pigment loss or any detrimental effect to the coating. About 10 mL of the pigmented latex was transferred to a spray bottle pressurized with nitrogen to about 30 psig (0.2 MPa). A small amount of the pigmented latex was sprayed onto a cementitious fiber board. A uniform coating of the cementitious fiber

board was obtained. Again, after about 1 minute, the coated board was placed under a stream of running water. There was no indication of pigment loss or any detrimental effect on the coating.

Example 3 - Forming a Fast-Setting Coating on Base-Treated Filter Paper

5           A 9.0-cm circle of Whatman #1 qualitative filter paper was cut into a 5.7 cm by 7.0 cm rectangle, then taped to a glass plate along all edges. The paper was soaked with a saturated sodium bicarbonate solution, then blotted with paper towels to remove excess fluid. A coating of latex having a composition described in Table II was then spread on the coated paper. Rapid setting of the latex film on the paper was apparent in less than  
10       15 seconds. After about 2 minutes the coating was completely dry-to-the-touch. After 3 minutes, a drop of water was placed onto the coated paper and beaded with no visible signs of bleeding. This drop test was repeated several times with the same results.

Example 4 - Forming a Fast-Setting Coating on Base-Treated Newspaper

15           An 11-inch by 17-inch (28-cm by 43-cm) sheet of paper was suspended in a hood and lightly sprayed with a 1.0 percent solids sodium bicarbonate solution, then allowed to dry overnight. The following day, the sample was coated with a thin layer of the latex having a composition described in Table II. The coating set in less than 10 seconds; it displayed no indications of bleeding into the paper, and it produced a glossy surface.

Example 5 - Forming a Fast-Setting Coating on Base-Treated Cloth

20           A swatch of common clothing material (60 percent cotton, 40 percent polyester) was dipped into a 1.0 percent by weight solution of sodium bicarbonate and allowed to soak for 5 minutes. The swatch was then removed, squeezed as dry as possible and taped to a glass plate. An 8-mil drawdown bar was then used to spread across the swatch, a sample of the latex having a composition described in Table II. The latex was dry-to-the-touch within  
25       10 seconds. Within 2 minutes, the excess water could be squeezed from the coated material using a high-pressure laminated plastic roller. Within 30 minutes the latex dried to a clear flexible coating with some level of gloss.

Example 6 - Plural Component Spraying with Alkaline Material

30           A Binks Mach 1 PCX Plural Component paint sprayer was used to apply a blended stream of a latex having a composition described in Table II, and a 3.0 percent by weight

- solution of  $K_2HPO_4$  to a sample of oak-laminated plywood. The atomizing pressure was set at about 72 psig (0.50 MPa) and both storage vessels were set at approximately 35 psig (0.24 MPa). The coating became dry-to-the-touch rapidly (less than 30 seconds). Two aluminum coupons (Q-panel, Inc.) were also coated with similar results. The atomizing pressure was decreased to 45 psig (0.31 MPa) and the storage vessels pressure dropped to 10 psig (0.07 MPa). The procedure was then repeated. The rate at which the coating became dry-to-the-touch was unaffected, but the surface of the coating was improved. A "Cold Rolled Steel" coupon (Q-panel) was also coated easily using the same operating conditions and obtaining similar results.

#### 10 Example 7 - Plural Component Spraying Using an Anionic Latex

The paint sprayer described in Example 6 was used to apply a blended stream of a latex having a composition described in Table II, and an anionic latex having a composition described in Table IV.

Table IV

Monomer	Weight Percent	Mole Percent
Butyl Acrylate	50.5	43.9
Methyl Methacrylate	43.0	47.9
Methacrylic Acid	5.95	7.7
Allyl Methacrylate	0.52	0.46

- 15 The atomizing pressure was set to 40 psig (0.30 MPa) and the storage vessel pressure was set to 7.5 psig (0.05 MPa). The spray was applied to a glass plate and the resultant coating set in less than 30 seconds.

#### Example 8 - Plural Component Spraying with an Anionic Material

- 20 The paint sprayer described in Example 6 was used to apply a blended stream of latex, having a composition described in Table II, and an aqueous anionic corrosion inhibiting solution, consisting of 4.45 percent by weight of MIRANOL CS® (manufactured by Rhône Poulenc). The atomizing pressure was set at 35 psig (0.24 MPa) and the storage vessel pressures were set at 5 psig (0.03 MPa). The coating was applied to an untreated aluminum coupon, a pre-treated aluminum coupon (Q-panel, Inc.) and a pre-coated sample

of PTO. The spray formed an acceptable coating and set in less than 30 seconds on all three test panels.

**Example 9 - Plural Component Spraying with Cationic Latex and Anionic Latex**

The paint sprayer described in Example 6 was used to apply a blended stream of cationic latex, having a composition described in Table V, and an anionic latex, having a composition as described in Table IV. The atomizing pressure was set at 35 psig (0.24 MPa) and the storage vessel pressures were set at 10 psig. The coating was applied to an untreated glass plate. The spray formed an acceptable coating and coacervated in less than 20 seconds. It set in less than 30 seconds. The plate was placed under running water after 1 minute with no detrimental effect to the coating. Two aluminum coupons, one of which was pre-treated with phosphate (Q-panel, Inc.), were also coated. The spray formed an acceptable coating and coacervated in less than 15 seconds on both test panels.

Table V

Monomer	Weight Percent	Mole Percent
Butyl Acrylate	56.2	51.3
Methyl Methacrylate	39.7	46.5
M-Quat	4.1	2.3

## CLAIMS:

1. A coated material comprising a substrate having a surface and a coating thereupon, wherein the coating is prepared by any of the steps of:

- 5                   a) contacting the surface of the substrate with a stable aqueous dispersion that contains a polymer having pendant strong cationic groups, and pendant weak acid groups; or
- 10                   b) contacting the surface of the substrate with a stable aqueous dispersion that contains a first polymer having pendant strong cationic groups, and a stable aqueous dispersion of a second polymer having pendant weak acid groups, the contact of the polymers with the surface being made in any order or concurrently;

15                   with the proviso that when the coating is prepared by the method of (a), the surface of the substrate is, or is treated to be, sufficiently basic that the stable aqueous dispersion sets in less time than the time required for a latex that only contains pendant strong cation groups or pendant weak acid groups to set.

2. The coated material of Claim 1 which is prepared by contacting the surface of the substrate with a stable aqueous dispersion that contains a polymer having strong cationic group, and weak acid groups.

20                   3. The coated material of either of Claims 1 or 2 wherein the polymer further has structural units formed from the polymerization of a non-interfering polymerizable monomer.

25                   4. The coated material of Claim 3 wherein the non-interfering polymerizable monomer is methyl acrylate, ethyl acrylate, butyl acrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, allyl acrylate, glycidyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, allyl methacrylate, glycidyl methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, a C<sub>3</sub>-C<sub>18</sub>-perfluoroalkyl methacrylate, a C<sub>3</sub>-C<sub>18</sub>-perfluoroalkyl acrylate, a C<sub>3</sub>-C<sub>18</sub>-perfluoroalkyl vinylbenzene, styrene,  $\alpha$ -methylstyrene, or vinyltoluene, or a combination thereof.

5. The coated material of any of Claims 1, 2, or 4 wherein the weak acid groups are formed from the polymerization of acrylic acid, methacrylic acid, itaconic acid,  $\beta$ -carboxyethyl

acrylate, vinylbenzoic acid, vinylchlorophenol, vinylbromophenol, vinylthiophenol, or 2-propenoic acid: 2-methyl-, (hydroxyphosphinyl) methyl ester, or a combination thereof.

6. The coated material of any of Claims 1, 2, or 4 wherein the strong cationic groups are formed from either of:

- 5 a) the polymerization of a trialkylammoniumalkyl acrylate; a trialkylammoniumalkyl methacrylate, a trialkylammoniumalkyl acrylamide, a dialkylsulfonium salt, a benzylsulfonium salt, a cyclic sulfonium salt, a 2-methacryloxyethyltri-C<sub>1</sub>-C<sub>20</sub>-alkyl-phosphonium salt, a 2-methacryloxy-ethyltri-C<sub>1</sub>-C<sub>20</sub>-aralkyl-phosphonium salt, a 2-methacryloxyethyltri-C<sub>1</sub>-C<sub>20</sub>-aryl-phosphonium salt, a tri-C<sub>1</sub>-C<sub>18</sub>-alkyl-vinylbenzylphosphonium salt, a tri-C<sub>1</sub>-C<sub>18</sub>-aralkyl-vinylbenzylphosphonium salt, a tri-C<sub>1</sub>-C<sub>18</sub>-aryl-vinylbenzylphosphonium salt, a C<sub>3</sub>-C<sub>18</sub>-alkenyltrialkyl-phosphonium salt, a C<sub>3</sub>-C<sub>18</sub>-aralkyl-phosphonium salt, or a C<sub>3</sub>-C<sub>18</sub>-aryl-phosphonium salt; or
- 10 b) the polymerization of a polymerizable tertiary amine or sulfide followed by reaction with an alkylating reagent to form a quaternary ammonium salt or a sulfonium salt; or
- 15 c) the polymerization of a polymerizable monomer containing an electrophilic group, followed by the reaction with a tertiary amine or a sulfide to form a quaternary ammonium salt or a sulfonium salt.

20 7. The coated material of Claim 4 wherein the non-interfering polymerizable monomer is methyl methacrylate, butyl acrylate, styrene, 2-hydroxyethyl methacrylate, 4-methacryloxy-2-hydroxy-benzophenone, or 2-(2'-hydroxy-5-methacryloxy-ethylphenyl)-2H-benzotriazole, or a combination thereof.

25 8. The coated material of Claim 4 wherein the ratio of the structural units formed from the non-interfering polymerizable monomer to the strong cationic groups and the weak acid groups is from 90:10 to 99.5:0.5, and wherein the strong cationic groups are formed by the polymerization of an ethylenically unsaturated quaternary ammonium salt associated with a chloride, bromide, nitrate, or sulfate counterion.

30 9. The coated material of Claim 8 wherein the quaternary ammonium salt is 2-[(methacryloyloxy)ethyl]trimethylammonium chloride; the weak acid groups are formed

from the polymerization of acrylic acid or methacrylic acid, or a combination thereof; and the non-interfering polymerizable monomer is styrene, methyl methacrylate, or butyl acrylate, or a combination thereof.

10. The coated material of any of Claims 1, 2, 4, 7, 8, and 9, wherein the substrate is  
5 cured Portland cement, uncured Portland cement, aluminous cement, inorganic mortar, or cementitious fiber board, or is treated to be basic and is metal, glass, paper, plastic, cloth, wood, or leather.

11. The coated material of any of Claims 1, 2, 4, 7, 8, and 9 wherein the surface of  
the substrate is contacted with a stable aqueous dispersion that contains a first polymer  
10 having strong cationic groups, and a stable aqueous dispersion of a second polymer having weak acid groups, the contact of the polymers with the surface being made in any order or concurrently, and wherein the pH of the first or the second stable aqueous dispersion is at least 5.

12. The coated material of Claim 11 wherein the first polymer further has weak acid  
15 groups.

13. A method of preparing a fast-setting coating on a substrate having a surface comprising either of the steps of:

a) contacting the surface of a substrate with a stable aqueous dispersion  
containing a polymer having pendant strong cationic groups, and pendant  
20 weak acid groups; or  
b) contacting the surface of the substrate with a stable aqueous dispersion  
containing a first polymer having strong cationic groups, and a stable aqueous  
dispersion of a second polymer having weak acid groups, the contact of the  
polymers with the surface being made in any order or concurrently;  
25 with the proviso that when the water-resistant coating is prepared by the method of (a), the surface of the substrate is, or is treated to be, sufficiently basic so that the stable aqueous dispersion sets in less time than the time required for a latex that only contains pendant strong cation groups or pendant weak acid groups to set.

14. A stable aqueous dispersion comprising a polymer having strong cationic  
30 groups, weak acid groups, and structural units formed from the polymerization of a non-

interfering polymerizable monomer, wherein the ratio of structural units formed from the polymerization of the non-interfering polymerizable monomer to the strong cationic groups and the weak acid groups is from 70:30 to 99:1, with the proviso that the strong cationic groups are associated with a non-alkaline counterion.

## INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/US 98/09707

## A. CLASSIFICATION OF SUBJECT MATTER

B 05 D 1/00, C 04 B 41/63, C 09 D 133/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B 05 D, C 08 F, C 09 D, C 04 B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0000426 A1 (THE UNIVERSITY OF MELBOURNE) 24 January 1979 (24.01.79), the whole document. --	1-14
A	EP 0239035 A2 (BASF AKTIENGESSELLSCHAFT) 30 September 1987 (30.09.87), the whole document. --	1-14
A	EP 0183158 A2 (THE DOW CHEMICAL COMPANY) 04 June 1986 (04.06.86), the whole document. ----	1-14

☐ Further documents are listed in the continuation of box C.☐ Patent family members are listed in annex.

## \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*&\* document member of the same patent family

Date of the actual completion of the international search

03 September 1998

Date of mailing of the international search report

06.11.98

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, T'x. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

BECK e.h.

# ANHANG

zum internationalen Recherchen-  
bericht über die internationale  
Patentanmeldung Nr.

# ANNEX

to the International Search  
Report to the International Patent  
Application No.

# ANNEXE

au rapport de recherche inter-  
national relatif à la demande de brevet  
international n°

PCT/US 98/09707 SAE 196077

In diesem Anhang sind die Mitglieder  
der Patentfamilien der im obenge-  
nannten internationalen Recherchenbericht  
angeführten Patentedokumente angegeben.  
Diese Angaben dienen nur zur Unter-  
richtung und erfolgen ohne Gewähr.

This Annex lists the patent family  
members relating to the patent documents  
cited in the above-mentioned inter-  
national search report. The Office is  
in no way liable for these particulars  
which are given merely for the purpose  
of information.

La présente annexe indique les  
membres de la famille de brevets  
relatifs aux documents de brevets cités  
dans le rapport de recherche inter-  
national visée ci-dessus. Les renseigne-  
ments fournis sont donnés à titre indica-  
tif et n'engagent pas la responsabilité  
de l'Office.

Im Recherchenbericht angeführtes Patentedokument Patent document cited in search report Document de brevet cité dans le rapport de recherche		Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
EP A1	426	24-01-79	AU A1 37473/78	21-02-80
EP A2	239035	30-09-87	AT E 54319	15-07-90
			CA A1 13229670	17-05-94
			DE A1 3609829	24-09-87
			DE CO 3763491	09-08-90
			EP A3 2339033	25-11-87
			EP B1 3339033	04-07-90
			JP A2 6222241	12-10-87
			NO A 8711175	20-03-87
			NO B 168831	30-12-91
			NO C 168831	08-04-93
			US A 4748330	31-03-88
			AT E 46331	15-09-89
			CA A1 1262299	14-11-89
			DE A1 3537457	23-04-87
			DE CO 3665594	19-10-89
			EP A1 3339033	06-03-87
			EP B1 3339033	13-09-89
			JP A2 62100508	11-05-87
			DE A1 3537455	23-04-87
EP A2	183158	04-06-86	AU A1 48978/85	28-05-87
			AU B2 592725	08-02-90
			CA A1 1262279	07-11-89
			CN A 85108570	30-07-86
			EP A3 183158	22-02-89
			JP A2 61130306	18-06-86
			KR B1 9105666	01-08-91
			ZA A 8508454	29-07-87